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⑨ FINAL TECHNICAL REPORT
FOR
NAVAL AIR SYSTEMS COMMAND
CONTRACT NUMBER N00019-79-C-0618 *new*
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LEVEL II

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TO STUDY THE RF PROPERTIES OF SUPERCONDUCTING A15 COMPOUNDS

By

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M. R. Beasley

T. H. Geballe

H. A. Schwettman

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PRINCIPAL INVESTIGATORS

W. W. Hansen Laboratories of Physics
Stanford University
Stanford, California 94305

⑪
July 1981

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I. SUMMARY

This is the final technical report for the Naval Air System Command
contract N00019-79-C-0618. The purpose of the work performed under this
contract was to study the low rf-field loss of A15 superconducting
compounds. This type of superconducting material has potential for
application to the construction of microwave energy storage cavities whose
energy can be dumped in a very short time so as to produce a very large
microwave power pulse. During the contract period an apparatus, using a
calorimetric technique, was developed to measure the surface resistance of
small-area superconducting samples deposited on sapphire substrates. Both a
Nb and a Nb_3Sn sample (the latter in the A15 structure) were prepared,
characterized and measured. These initial measurements revealed additional
losses that are most likely due to the region near the superconductor-sapphire
interface. Measurements of the superconducting transition temperature were
made as a function of film thickness to study the effect of the interface.
The interface losses can be avoided in practice, and in our measurements they
can be circumvented by employing a cicularly cylindrical geometry which
shields the interface region from the rf fields. This geometry has been
explored, and it may be implemented in the successor contract. In the course
of developing the surface resistance apparatus, dielectric loss measurements
were made on pure sapphire samples.

II. DEVELOPMENT OF APPARTUS TO MEASURE THE
RF SURFACE RESISTANCE CALORIMETRICALLY

Measurements of the surface resistance are conventionally carried out by observing the electrical Q of a cavity made from the material of interest, and by then computing the surface resistance from the observed Q and the known field distribution in the cavity. This conventional method of surface resistance measurements leads either to a rather complicted and large sample geometry or to other difficulties. Our effort has been directed toward developing an apparatus for measuring surface resistance of small samples of convenient geometries with which detailed material studies can be carried out. This apparatus uses a calorimetric technique to directly measure the rf power loss in the sample.

Figure 1 is a schematic of the apparatus which was developed for calorimetrically measuring the surface resistance. The apparatus consists of a copper cavity, the sample, and the calorimeter. The copper cavity is operated in the TE_{011} mode at 8.6 GHz and has a Q of $\sim 10^5$. The rf field in the cavity is determined from microwave measurements of the applied power, cavity Q , and coupling factor. A sample is placed along the axis of the cavity where the rf magnetic field is parallel to the sample and in the direction of the cavity axis. The rf electric field at the sample is relatively small for this mode. The sapphire on which the sample is deposited is thermally attached to the calorimeter in which the power loss is measured. Figure 2 shows a planar sample geometry and a circular cylindrical

X-BAND WAVEGUIDE,
ALSO USED TO EVACUATE
CAVITY AND CALORIMETER

SAPPHIRE ROD

SAMPLE COATED
ON SAPPHIRE
ROD

TE_{011} MODE
COPPER CAVITY

MAGNETIC
FIELD LINES

COPPER BLOCK WITH
Ge THERMOMETER
AND HEATER FOR
MEASURING POWER
LOSS

THERMAL
RESISTANCE

COPPER BLOCK WITH
Ge THERMOMETER
AND HEATER FOR
SETTING TEMPERA-
TURE OF SAMPLE

CALORIMETER
VACUUM
CONTAINER

FIG. 1--Microwave property measurement scheme.

0.5 mm

6.6 cm

sample

2 mm

3 mm

Rectangular

Circular
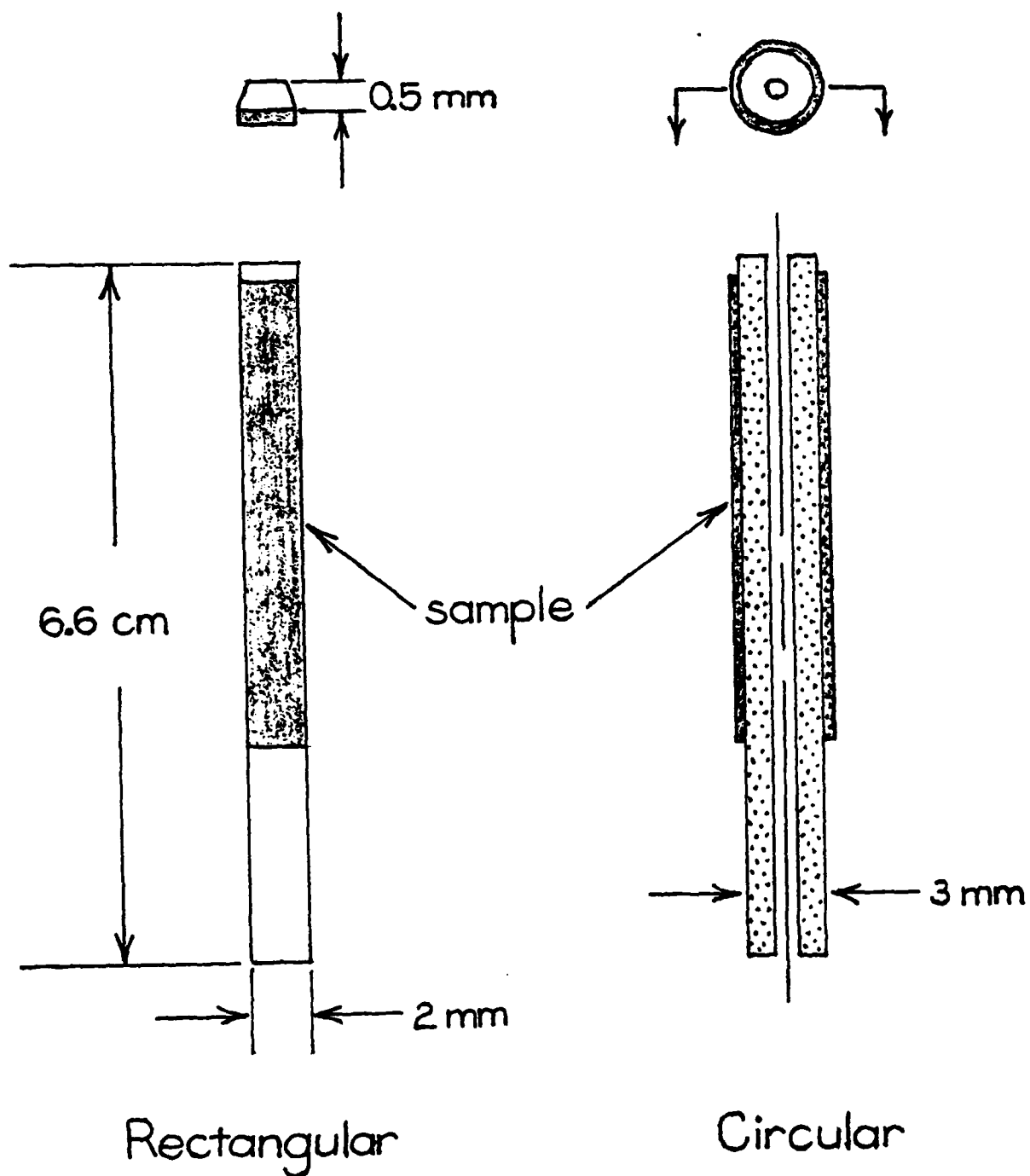
Fig 2. Substrate Geometry

sample geometry both of which can be used in the apparatus. The calorimeter
is enclosed in a can which is evacuated for thermal isolation.

Figure 3 is a schematic of the calorimeter. The heat sink is a helium
bath at temperature T_B which is typically set at either 1.2 or 4.2 K. A
copper block connected to the helium bath by the thermal resistance R_{T_0} is
raised above T_B to temperature T_0 by applying heat to the resistance
R_{H_0}. With $T_B = 1.2$ K, T_0 can be varied in the range of 1.4 to 20 K. The
temperature T_0 is measured with a calibrated Ge resistance thermometer
using an ac bridge at about 400 Hz and a phase-sensitive detector. Employing
R_{H_0} as a control element, T_0 is maintained with a stability on the order
of 1 μK. The second copper block at T_1 is approximately in thermal
equilibrium with the sapphire rod and sample. Any rf power dissipated in the
sample or power dissipated in R_{H_1} results in an incremental temperature
rise $\Delta T = T_1 - T_0$ which is typically a few mK or less. The thermal
resistance R_{T_1} is a smooth function of temperature and for small
ΔT one can write a linear approximation for the power loss P

$$P = \frac{\Delta T}{R_{T_1}(T_0)} = f(T_0)\, \Delta S \quad,$$

where ΔS is the change in output of the temperature detector due to P.
Applying a known power to R_{H_1} and observing ΔS yields a determination of
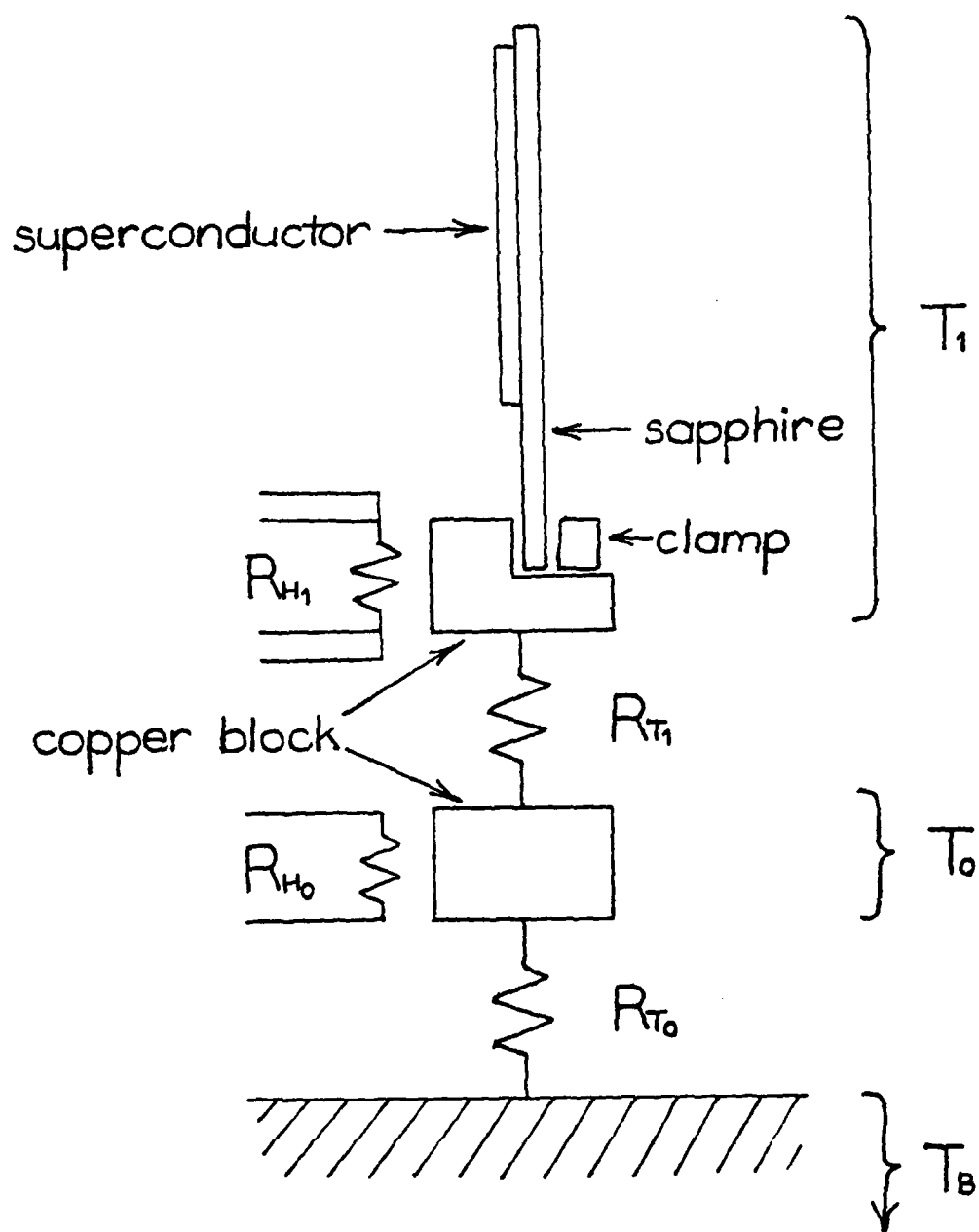$f(T_0)$. Thus a measurement of ΔS due to an applied rf field on the sample

Fig 3. Schematic of calorimetric apparatus

yields an absolute measurement of the rf power loss. An example of a measurement of ΔS is shown in Fig. 4

These calorimetric loss measurements require a modest amount of data collection and manipulation. For this reason a microcomputer is employed for the purposes of experimental control, data collection, and analysis. Figure 5 illustrates how a data point is typically measured. The calorimeter is set to some temperature T_0 , and it is allowed to come to equilibrium. The computer takes ten samples of signal S at intervals of two seconds (averaging time of lock-in detector is about 2 seconds) and then averages these ten samples to give S_0. The computer then turns on the heater power (or rf) at time t_1 and then waits for a time t_w before again taking a sample to give the average S_1. The wait time t_w is about 10 times the thermal relaxation time, which is in the range of 1 to 25 seconds for temperatures in the range 1.4 to 20 K. The computer then turns the heater power off at time t_2 , and continues in this manner until the values S_0 , S_1 , S_2 , S_3 and S_4 have been found. From these values a mean value of $\overline{\Delta S_H}$ is produced with the linear drift removed and also an estimate of $\sigma_{\overline{\Delta S_{H_1}}}$ is produced. $\overline{\Delta S}_{RF}$ and $\sigma_{\overline{\Delta S}_{RF}}$ are measured in the same manner.

This apparatus has been used to make surface resistance measurements of both Nb and Nb_3Sn and also to make measurements of the dielectric loss of sapphire. The surface resistance measurements can be made over a large dynamic range from 1 nΩ to 1 Ω , and the apparatus has the capability of a large range of applied rf field level. A set of measurements on a sample takes from two to three days to complete including mounting of the sample, transfer of liquid helium and the surface resistance measurement.

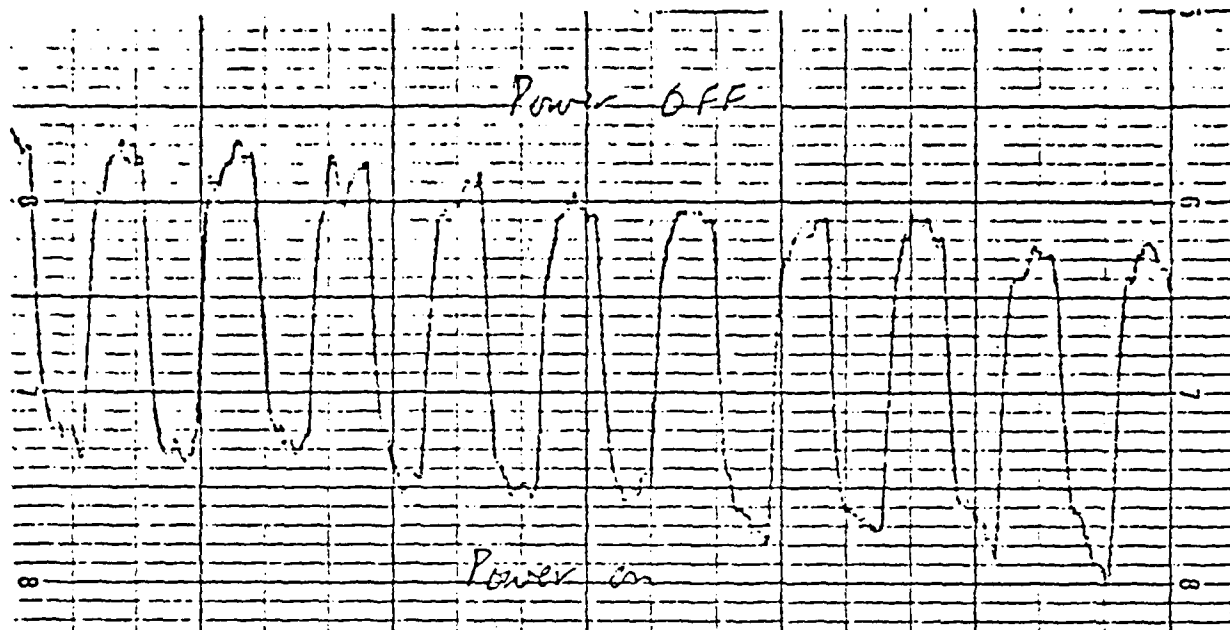FIG. 4--Signal showing the temperature change of the calorimeter
when a heat-power of 53 nW is turned on and off. The
heat power sensitivity of the calorimeter at 4.4 K is
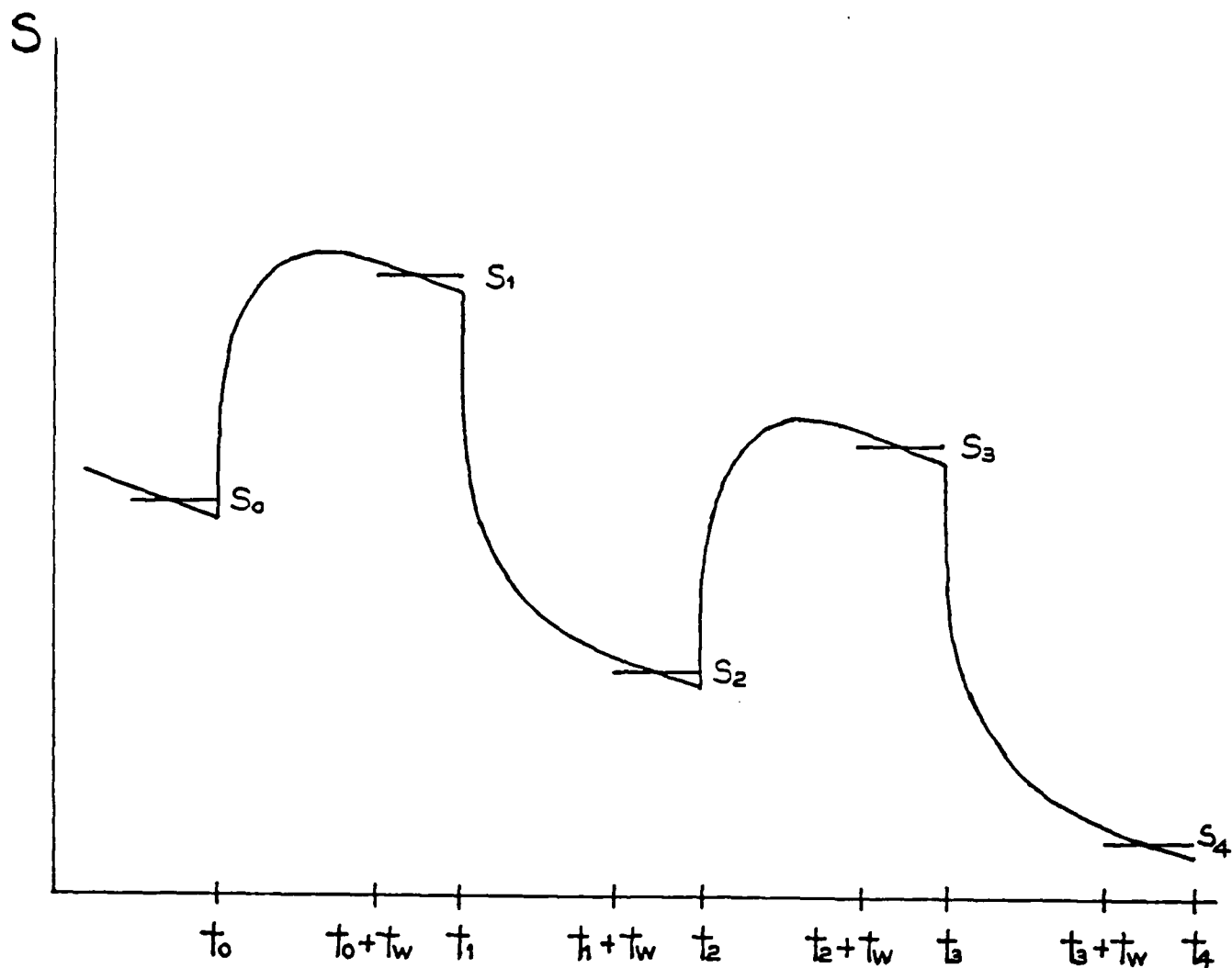about 4 nW, corresponding to a temperature change of
3 µK.

FIG. 5--Signal of temperature detector vs. time, illustrating
the time sequence for the measurement of the change in
the temperature of the calorimeter with application
of rf or heater power.

III. SAMPLE PREPARATION, CHARACTERIZATION AND MEASUREMENTS

The samples for this program are being produced using the existing multiple-electron beam coevaporation facility in the low-temperature group of the Ginzton Laboratory.[1] This facility has the capability for the simultaneous deposition of up to three elements on heated substrates. The specific deposition procedures employed use the techniques developed previously which have been shown to lead to good superconducting properties on the upper (vacuum) film surface through electron tunneling studies. The specific deposition parameters utilize are discussed for each case below.

A. Nb Film Preparation and Measurement

The first sample prepared was a Nb film which is simpler to prepare than the A15 compound Nb_3Sn. This (500 nm thick) Nb sample was used to test the preparation and measurement methods. The film was produced by evaporation of niobium in a 3×10^{-7} torr vacuum at the rate of 132 nm/min. on one side of a 2.0 x 0.5 mm rectangular sapphire substrate held at 500 C during the evaporation. The sample was then placed in the calorimetric apparatus for surface resistance measurements. The results of these measurements are shown in Fig. 6. Above 9.3 K, the surface resistance is nearly temperature independent, which would be expected in the normal state, and it is equal to 7.8 mΩ. This value implies an electron mean free path on the order of 50 nm. Below 9.3 K, the surface resistance first rapidly drops and then reaches an asymtotic value of 3.7 mΩ at 5 K. From the data we determine the superconducting transition to be 9.26 ± .03 K which is consistant with the
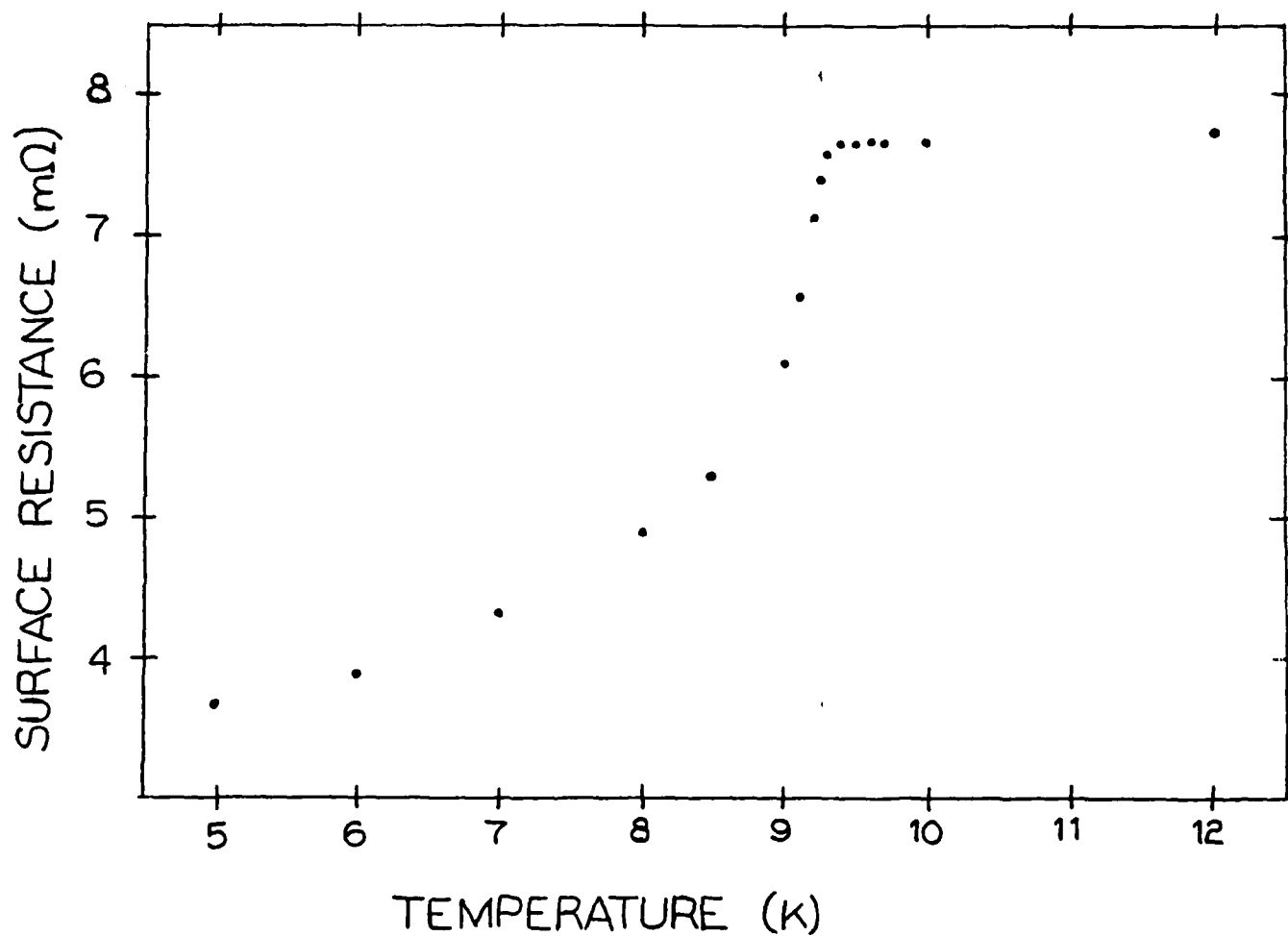
Fig 6. Surface resistance of niobium as a function of temperature

transition temperature of pure niobium. The only surprising and important
feature of the data is the relatively large asymtotic value of surface
resistance observed at 5 K. In fact since the surface resistance drops by
only about a factor of two from the normal state to the asymtotic value of 5 K
an interpretation may be that only one surface of the Nb layer is
superconducting. The suspect surface is the one at the sample/substrate
interface. This interpretation led us to the study of the interface described
in Section IV.

B. Nb_3Sn Film Preparation and Measurements

A 1.0 micro-meter thick Nb_3Sn film was prepared by coevaporating Nb and
Sn in a 1.2 x 10^{-7} torr vacuum at the rate of 184 nm/minute on a sapphire
substrate held at 700 C. The sapphire substrate was cleaned by heating it in
the vacuum to 900 C prior to the evaporation. After removing the sample from
the vacuum, it was clear, as expected, that there was a layer of tin
(reflected from the substrate holder during evaporation) located on the back
surface of the sapphire substrate, opposite to the Nb_3Sn film. It was decided
that the material on the back and sides of the sapphire substrate should be
removed. This was accomplished by ion beam milling these surfaces with argon
ions. This ion-beam milling was successful. However, substantial amounts of
zinc, copper, and nickel (verified by electron-beam microprobe) were
inadvertantly sputtered onto the top of the Nb_3Sn film by the ion beam. To
remove these elements the sample was dipped sequentially into the following
solutions which were agitated with an ultrasonic transducer: (1) nitric acid
for 15 minutes, (2) de-ionized water for 5 minutes, (3) hydrochloric acid for

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15 minutes, and (4) de-ionized water for 5 minutes. Both acid solutions were made from concentrated solutions mixed with an equal amount of de-ionized water. After the final rinse, the sample was dried with a stream of dry nitrogen gas.

The surface resistance data for this Nb_3Sn sample are shown in Fig. 7 for the temperature range from 1.5 to 18 K. The surface resistance improves by a factor of 1600 from 380 milli-ohm at 18 K in the normal state to 240 micro-ohm at 1.5 K in the superconducting state. There are two relatively abrupt jumps in the surface resistance: one at 17.5 K associated with the A15 structure Nb_3Sn superconducting transition, and one at 3.0 K possibly associated with an amorphous Nb_3Sn transition. Approximately 10% of the losses at the lowest measured temperature are estimated to be in the sapphire dielectric. This conclusion is based on the measurement of losses in a bare sapphire rod.

Also shown in Fig. 7 is a curve of the surface resistance computed from the formulation of Mattis and Bardeen for a BCS superconductor. This formulation has been shown to reproduce the measured surface resistance of tin, lead, niobium, and other superconductors with a substantial degree of precision. The computed surface resistance plotted in Fig. 7 assumes parameters which approximately describe Nb_3Sn, and in particular the transition temperature was chosen to be 18 K. From a comparison of the computed and measured curves in Fig. 7, a general observation is that the structure of the measured surface resistance is substantially more complex than that for the computed surface resistance. This result suggests that the physical structure of the Nb_3Sn film may also be complex. In any event the reduction of the loss by a factor of ~ 2000 in our first attempt is very encouraging and apparently shows that the sample substrate interface problems are less severe for Nb_3Sn than for Nb.
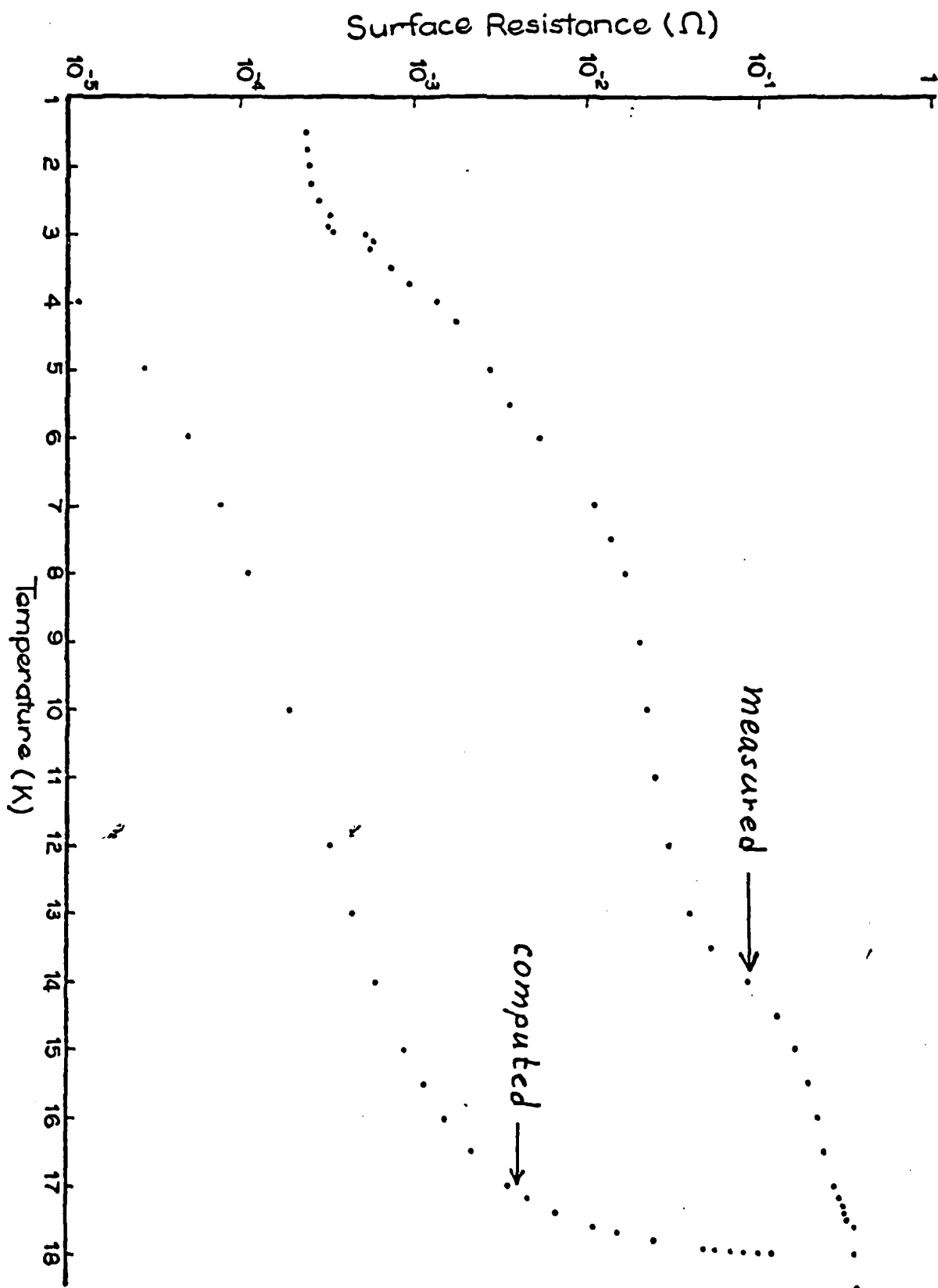
Figure 7.   Surface Resistance of Nb$_3$Sn Film as a Function of Temperature.

C.   Chemical and Microstructural Analysis of Nb₃Sn Film

After the specimen was removed from the test apparatus, it was
characterized by scanning electron-beam microscopy (SEM) and by electron
microprobe analysis. The electron microprobe analysis consisted of the
measurement of the elemental concentration at nine equally spaced regions
(about 5 mm apart) along the film. This analysis indicated that the
composition is uniform to within 0.1 atomic percent which is better than the
absolute microprobe resolution (~ 1.5 atomic percent), and that the average
atomic percent of Sn is 25.3 with the remainder being Nb. The perfect
composition would be 25.0 atomic percent Sn. From past experience with this
type of measurement it appears that such measurements are high by about one
atomic percent, and thus the corrected composition should be about 24.3 atomic
percent. This is consistent with the transition temperature of 17.5 K given
above.

The SEM analysis shows a uniform, smooth deposit except for the features
given below:

(1)   The edges of the sapphire were chipped during the polishing
       operation by the vendor. The deposit has coated these chipped
       regions, leading to a certain amount of film surface that is not
       parallel to the rest of the film, and the possibility exists that
       the composition in these regions is not the desired value, thus
       giving a lowered transition temperature. In addition, the ion-
       beam milling of the sides was not done for a long enough time to
       remove completely this material, and has very likely disordered
       the crystalline film material in these regions. This would lead
       to a lowered transition temperature in these regions.

(2)   Irregular shaped projections above the film surface were found
       (about 12 over the entire surface). These ranged from 5 to 50
       micro-meter in general size, and x-ray analysis in the SEM
       indicated that the Nb-Sn film was deposited over them (there also
       occasionally appeared uncoated particles containing silicon).

(3)   Similarly shaped holes in the film were also found (about ten
       over the entire surface). X-ray analysis showed that the bottom
       was sapphire. The columnar growth morphology of the Nb_3Sn was
       evident in the walls of the hole. We speculate that the holes
       are a result of the removal of the particles discussed above
       after the Nb_3Sn deposition. In a few cases it appears that part
       of the removed particle is left behind at the edge of the hole.
       X-ray analysis in the SEM did not reveal the chemical elements of
       this material. We note that elements lighter than Mg are not
       observable by this technique, and that the polishing compound
       used to polish the sapphire is diamond.

The exposed walls around the holes provide a view of the growth
morphology of the Nb_3Sn deposit. It appears that the columnar size is in the
range of 80-100 nm. This dimension is seen both in the side view (the walls)
and in the structure evident in the surface. In previous research, we have
compared similar evidence using both SEM and transmission electron microscopy
and have found that the SEM can be misleading sometimes.[2] Thus the present
information should be taken in that vein, and further work may be desirable.
On the other hand the indicated size of the columnar growth is not
unreasonable for the conditions of substrate temperature and rate of
deposition. In short, some non-idealities of the films have been identified
and can be easily avoided by improved deposition procedures.

IV. SUPERCONDUCTOR - SUBSTRATE INTERFACE CONSIDERATIONS

As discussed above there is evidence for excessive losses at the sample/substrate interface of our thin film samples. We have investigated various possibilities for the origin of these losses. Chief among these has been the possibility of a surface region of deteriorated superconductivity. Several possible origins for such a region are discussed below.

A. Past Results Showing T_c Reduction In Nb and Nb_3Sn Thin Films

One experimental approach to exploring the properties of the sample/substrate interface is to study the properties of very thin films on the substrate. This is attractive because it is relatively simple to do, although it must be recognized that the properties of very thin films may not relate exactly to the interface region of thicker films. Moreover there is some useful information available in the literature.

We are aware of two studies of the thickness dependence on T_c of niobium. Mayadas, Laibowitz and Cuomo[3] of IBM studied both sputtered and electron beam evaporated Nb films, using sapphire substrates and a substrate temperature of ~ 550 C. Their work was unique in that they established that the films were single crystals. Similar studies were made by Wolf, Kennedy and Nisenoff[4] of NRL. They sputtered Nb onto fused quartz and glass at ambient temperatures.

These researchers interpreted their results in terms of a proximity effect model in which the superconductivity of the whole film is diminished

due to the proximity of a highly degraded surface layer (of thickness a) in which the superconducting interaction has gone to zero. According to Cooper the transition temperature of such a film as a function of temperature is $T_c(d) = T_c(\infty) \exp(-2a/NVd)$ where NV is the superconducting interaction strength and d the film thickness. According to this prediction a plot of log $T_c(d)$ vs. d should be a straight line with a slope determined by a . As shown in Fig. 8 their data fits such a prediction fairly well and yields a valule of a $\simeq$ 5.8 Å.

We have carried out a similar analysis of our own Nb films as discussed below. In addition to this work on Nb , we also have preliminary results on films of Nb_3Sn. These results will not be discussed further, except to state now the main results: for Nb_3Sn both T_c and Δ (energy gap) start to decrease for thicknesses less than ~ 1000 A. This is approximately twice the thickness for which Nb shows a decrease.

B.   Dependence of the T_c of Nb on Film Thickness and Substrate Preparation

Nb was deposited at a rate of 22 Å/sec at a total vacuum of 1.3 x 10^{-7} torr. On the basis of residual gas analysis this vacuum consisted of the masses 2, and 16 in about equal amounts, and 18, 28, and 44 all at ~ 1/3 of these. The substrates were cleaned using our standard proceedure. Before the deposition the substrates were heated in the deposition chamber to 900 C for 2 hours at a total pressure of ~ 10^{-7} torr. The niobium was also outgassed during this time. The substrate temperature during the deposition was ~ 500 C. Three rows were exposed for each thickness (determined by the shutter opening time). For purposes of comparison row A contained sapphire
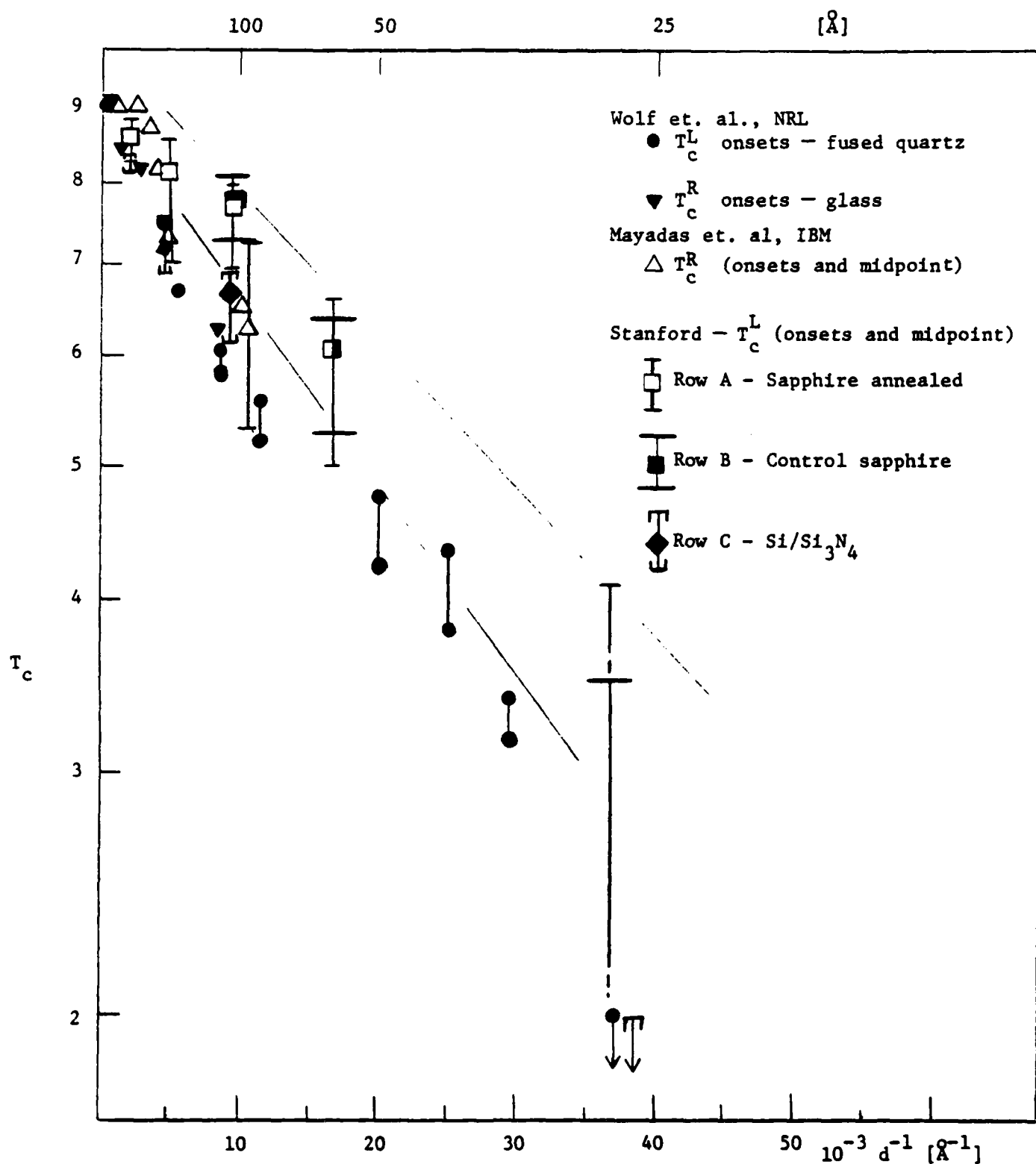
FIG. 8--T_c vs. the reciprocal film thickness
of niobium films on various substrates.

substrates that had previously been baked and outgassed at 1200 C for 48 hours at a vacuum of 1 x 10^{-8} torr. Row B held a control set of unbaked sapphires, and Row C consisted of Si with 500 A of Si_3N_4. A 50 A thick Si (amorphous protective coat was deposited on all of the films after they had colled to less than 100 C.

The results are shown in Fig. 8 along with the IBM and NRL results.

1. The advantage of annealing the sapphire at 1200 C is slight. The biggest effect is at the thinnest film (0.5 K at 27 A).

2. There is a large substrate effect. Si/Si_3N_4 and fused quartz (NRL) both yield lower T_c's than sapphire. This is likely explained as due to strains arising from differences in the differential thermal expansion.

3. Our measurements are in general agreement with the NRL and IBM results:

    a. In terms of a Cooper-proximity layer model outline above, the decrease in T_c can be described as due to ~ 5-6 A of normal material on both sides of the film.

    b. Our T_c's are slightly higher than those found in the IBM and NRL studies. The IBM work is more comparable in terms of substrate material and temperature. Unfortunately, their data is limited to the thicker films. It is noteworthy that their Nb films were single crystal.

A number of other experiments were done that add some additional semiquantitative information. A series of experiments were made to compare samples deposited at different substrate temperature. T_s's of 700, 500, and ~ 200 C were compared by depositing a row of samples at each temperature using a moving shutter. The thickness along the row varied from ~ 0 to ~ 500 A,

and across each 1/4 x 1/4 sapphire by ~ 100 Å. The results indicate no large difference in T_c, with perhaps the 500 C row having a slight advantage. These substrates were also heated to ~ 900 C for about 2 hours before deposition.

Another experiment was carried out to see if a possible reaction with the sapphire or impurities in the sapphire could be prevented by pre-coating (without exposure to air) the sapphires at 700 C with ~ 500 Å of MgF_2. Also, as was done of the other films discussed in this report, about 50 Å of Si was deposited on top of the Nb after the substrates had cooled below 100 C. The T_c data show no significant difference as compared to a control group. These films are in the process of being chemically analyzed using Auger profiling. One preliminary result is that the MgF_2 pre-coat may have resulted in single crystal Nb, whereas the control Nb without MgF_2 does not show crystallographic orientation.

C. T_c Deterioration at an Interface

Below we enumerate a number of other reasons for T_c to decrease as the interface is approached.

1. Strains in the film-interface due to differential expansion between the substrate and deposit. We have already noted above that this could be the mechanism by which T_c decreases faster when on substrate with a low expansion coefficient like fused quartz, glass, and Si/Si_3N_4. Although sapphire is fairly well matched to NB, some strain could remain.

2. Chemical poisoning from the substrate including impurities in the substrate. Our past experience with Nb_3Ge (SIMS profiling) and Nb_3Sn

(Auger profiling) leads us to suspect that this could be important. Further Auger profiling is in progress in collaboration with the China Lake Michelson Laboratory group under Dr. V.Rehn. A normal layer 5-6 A thick due to chemical effects can explain the T_c vs. thickness data. However, the residual rf loss results on both the Nb and Nb_3Sn seem to require a more extensive normal layer. The residual losses for Nb_3Sn were much lower than for Nb and it is not yet clear how deep a normal layer would be required to explain this case.

3. Modification of the phonon density due to the interface, such as a stiffening or pinning of soft modes. These more exotic effects are possible but have not been investigated.

4. Effect of surface scattering on the electronic structure.

5. Gradient in the chemical composition (e.g. deviations from stoichiometry) of the main elements in a compound such as Nb_3Sn at the interface. In addition to more subtle causes for this, a very real one is that the sticking coefficient of Sn is very temperature dependent at the temperature of deposition used, and the temperature of the long sapphire rod was not held constant, particularly during the initial phase of the deposition. Recent experience on some of our other research programs also show that such thermal problems do arise when the sapphire is not in good contact with a substrate-holder. The sapphire is initially transparent to the thermal radiation. As it receives a film coating the temperature rapidly changes. The result is a gradient in the composition which causes

the T_c to change by several degrees near the surface. The solution will be to re-design the holder to insure a better temperature control.

V. SAPPHIRE LOSS MEASUREMENTS

Dielectric loss measurements were made on the sapphire substrates to determine if the losses in the sapphire would be low enough so as not to interfere with the loss measurements of the A15 layers. RF losses were made for two different sapphire samples: a 2.5 mm diameter rod supplied by Linde and a 2.0 x 0.5 mm rectangular rod supplied by Adolf-Meller, Inc. For the loss measurements, these rods were located along the axis of the TE_{011}-mode cavity. In this location, the principal rf field is a magnetic field parallel to the axis of the rod. The rf power loss in the sapphire was measured with the calorimeter discussed earlier. The measured losses are assumed to be the result of the magnetic field rather than the rather small electric field, and thus the losses have been characterized by a magnetic loss factor δ_M which is defined as the ratio $P_s/(\omega_o V_M)$: P_s is the power loss in th e sample, ω_o is the angular frequency of the applied rf field, and V_M is the peak instantaneous magnetic energy stored in the volume of the sapphire sample. The δ_M's for the round and rectangular rods are 2.48×10^{-6} and 1.24×10^{-6}, respectively. Magnetic loss factors are much larger than expected, by about a factor of 100, based on the results of Braginsky.[6] Nonetheless, these loss factors have been adequate for the first series of surface resistance measurements on Nb and Nb_3Sn.

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